PATENT ABSTRACTS OF JAPAN

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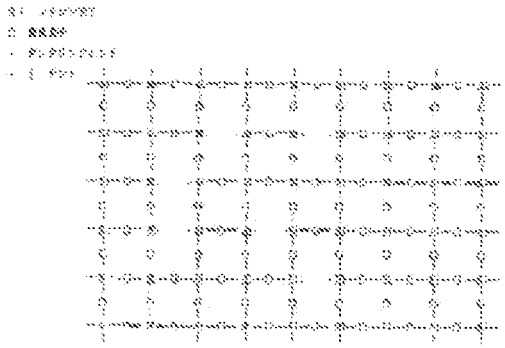
(54) SILICON OXIDE FILM ELECTRET



(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a long-life silicon oxide film eleletret by using a silicon oxide film contg. Si atoms each coupled with three oxygen atoms and having a dangling bond.
SOLUTION: A silicon oxide film composed of Si atoms mostly each coupled with four oxygen atoms contains Si atoms each coupled with three oxygen atoms and having a dangling bond (≡Si.or.Si≡). The dangling density is approximately 1013-1019cm-3 and the number of oxygen atoms is less than twice the number of Si atoms. This provides a long-life silicon oxide film electret good in heat resistance.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the silicon oxide electret which consists of electrically electrified silicon oxide.

[0002]
[Description of the Prior Art]Conventionally, the electret which is an insulator layer which has a permanent electric charge is used for the electrostatic microphone, the electrostatic relay, etc. Although an organic (polymer) material is used as a conventional electret material, By recent years, in order to attain thin-film-izing and a miniaturization of electret using the ultra-fine processing technology of semiconductors, such as IC-LSI, silicon oxide electret is examined as what is replaced with the polymer electret which consists of organic materials.
[0003]Silicon oxide electret is compared with polymer electret, (1) (2) thin-film(for example, 10 micrometers or less in thickness)-ization which has good electrifying stability also at an elevated temperature, [easy] (3) It has an advantage of ** which can be formed easily (in the case of a thermal oxidation method on a silicon substrate) on a substrate according to the conventional semiconductor manufacturing processes, such as a thermal oxidation method, plasma CVD method, and an LPCVD method.
[0004]
[Problem(s) to be Solved by the Invention]By the way, the life expectancy of the conventional silicon oxide electret is about several months, and there was a problem that it was shorter than the life of polymer electret. Then, as a means to increase the life expectancy of silicon oxide electret, before electrifying silicon oxide electrically, the art of processing said silicon oxide chemically by hexamethyl JISHIRANZAN (HMDS) is proposed, but. This art has bad controllability and reproducibility, and there is also little enhancement effect of a life expectancy.
[0005]For this reason, before electrifying electrically the silicon oxide formed on the silicon substrate by the thermal oxidation method, The art of carrying out annealing (preheating) of the silicon oxide is proposed (the 7 th international symposium on electrets (1991) 663,668). However, by having preheated, a life expectancy (life expectancy) did not increase remarkably and there was a problem that the electrifying stability of silicon oxide EKUTO let might be reduced with this preheating.
[0006]Succeeding in this invention in view of the above-mentioned reason, the purpose is to provide long-life silicon oxide electret.
[0007]
[Means for Solving the Problem]An invention of claim 1 to achieve the above objects in silicon oxide, It is what a silicon atom which combines with three oxygen atoms and has a dangling bond exists, and is characterized by things, When a dangling bond exists, an electronic state in a gap is made near the Fermi energy of an approximately center of a band gap, Since an electric charge is electrically fixed to a dangling bond which is making an electron energy level of this electronic state as a result, silicon oxide electret good [heat resistance] and long lasting can be provided.
[0008]Since dangling bond densities are abbreviated $10^{15}cm^{-3}$ thru/or abbreviated $10^{19}cm^{-3}$, an invention of claim 2, An electric charge is electrically fixed to a dangling bond which an electron energy level of this electronic state is made near the Fermi energy, and is making an electron energy level of this electronic state, and, as a result, heat resistance can provide good and long lasting silicon oxide electret.
[0009]Since an invention of claim 3 is twice [less than] the number of silicon atoms, the number of oxygen atoms, By forming a dangling bond of silicon, an electronic state in a gap is made near the Fermi energy of an approximately center of a band gap, An electric

charge is electrically fixed to a dangling bond which is making an electron energy level of this electronic state, and, as a result, heat resistance can provide good and long lasting silicon oxide electret.

[0010]Since an invention of claim 4 is the abbreviated 1.7 time of the number of silicon atoms, the number of oxygen atoms. An electric charge is electrically fixed to a dangling bond which the number of silicon atoms becomes superfluous to an oxygen atom, a dangling bond is formed, and an electronic state in a gap is made near the Fermi energy of an approximately center of a band gap, and is making an electron energy level of this electronic state. As a result, silicon oxide electret good [heat resistance] and long lasting can be provided.

[0011]In an invention of claim 1, since an invention of claim 5 contains hydrogen or nitrogen, it can increase a dyeing ring bond by heat-treating. In an invention of claim 3, since an invention of claim 6 is carrying out the abbreviated 1 atomic-ratio owner of the impurity of abbreviated 10 atomic ratios and nitrogen, an impurity of hydrogen, In order a part of H and N are contained in a form which carried out electrification and to fulfill neutrality condition, a dangling bond of silicon carries out electrification and an electric charge is fixed to a dangling bond. As a result, silicon oxide electret good [heat resistance] and long lasting can be provided.

[0012]

[Embodiment of the Invention]The mimetic diagram of the situation of combination of the silicon oxide electret of this embodiment is shown in drawing 1. Here, "-" in drawing 1 shows the dangling bond (uncombined hand) of the silicon atom (Si). The silicon oxide electret of this embodiment, As shown in drawing 1, in the silicon oxide which many of silicon atoms combine with four oxygen atoms (O), and is constituted, It is in the silicon atom (the silicon atom which has a dangling bond is hereafter described as "**Si-" or "-Si**") which combines with three oxygen atoms and has a dangling bond existing. For this reason, the silicon oxide electret of this embodiment, Since the electronic state in a gap is made near Fermi energy when the dangling bond exists. An electric charge is electrically fixed to the electron energy level of this electronic state, and it is got blocked, An electric charge is captured by the dangling bond (trap), as a result if a high temperature is not applied, it is not discharged, but heat resistance is good and the silicon oxide electret with which electric charge holding power has the long lasting large electret characteristic is obtained.

[0013]In drawing 1 and below-mentioned drawing 2, drawing 3, and drawing 9, although structure of the shape of a two-dimensional tetragonal lattice is used typically, four oxygen atoms enclose the surroundings of the silicon atom in regular tetrahedron structure in practice, and it has the structure where such a tetrahedron is mutually connected via the oxygen atom of a corner. By the way, since the oxygen atom has two joint hands [silicon atom / four joint hands], respectively, combination of pure silicon oxide (SiO_2) has structure as shown in the mimetic diagram shown in drawing 9. On the other hand, in the silicon oxide electret of this embodiment, As it has a dangling bond of a silicon atom and is shown in drawing 2, the structure which hydrogen oxide (OH) and nitrogen oxide (ON) combined with this dangling bond may be sufficient, and the thing of the structure which the hydrogen atom (H) and the nitrogen atom (N) combined may be used. H and O may exist between atoms.

[0014]Hereafter, the manufacturing method of the above-mentioned silicon oxide electret

is explained. First, the silicon oxide which has a dangling bond of a silicon atom is formed on the substrate which consists of materials on a silicon substrate or other than silicon. Here, silicon oxide can be formed by what is called the thermal oxidation method for putting a silicon substrate in high-temperature-oxygen atmosphere, and growing up silicon oxide, when a substrate is a silicon substrate. As a thermal oxidation method, what is called a wet oxidation style grown up in the oxygen gas containing moisture (H_2O) and which method of what is called a dry oxidation method make it grow up in the oxygen gas with which the high grade got dry may be used. In using the substrate which consists of materials other than silicon, The material gas (for example, mono-silane:SiH_4) containing Si and the material gas (for example, nitrous oxide:N_2O) containing oxygen can be supplied in the gaseous phase, and it can form with what is called a CVD method that decomposes each material gas and makes silicon oxide deposit on a substrate. Of course, silicon oxide may be deposited with a CVD method on a silicon substrate.
[0015]In order to deposit silicon oxide with a CVD method. For example, in the parallel plate type plasma CVD device 30 as shown in drawing 4, While holding the substrate 2 on the grounded lower electrode 32 and introducing material gas (for example, SiH_4 and N_2O) in the reaction chamber 31 of a reduced pressure state via the gas inlet 33, Plasma is generated and the silicon oxide 1 is made to deposit on the substrate 2 by impressing the high frequency voltage whose frequency is 13.56 MHz to the upper electrode 34 from RF generator AC. The chemical reaction at this time is described as follows, for example. $SiH_4+2N_2O->SiO_2+2H_2+2\uparrow N_2$ here, Compared with the time of being a gas mass flow ratio which can form the SiO_2 film suitable for stoichiometry, by supplying SiH_4 gas superfluously to N_2O gas, SiO_2 -- what is called silicon -- it changes into the state of being rich (Si-rich), and the dangling bond of a silicon atom (changing into the state where it is got blocked and oxygen atoms are insufficient) is formed. At this time, the number of the oxygen atoms in the silicon oxide 1 is twice [less than] the number of silicon atoms. By the way, since the above-mentioned silicon oxide 1 runs short of oxygen atoms at the time of deposition, It is generated by the dangling bond of a silicon atom and become easy to mix H of SiH_4 gas, N of N_2O gas, etc. in this dangling bond as an impurity (autodoping becoming is easy to be carried out), Interstitial atoms of Si-OH, Si-H, Si-ON, Si-N, etc., such as combination, H, and N, are included.
[0016]Formation of the silicon oxide in a CVD method may not be limited to plasma CVD method, and may be formed with the LPCVD method etc. which carry out the pyrolysis of the material gas by a reduced pressure state, and are made to deposit on a substrate for example. After forming the silicon oxide 1 on the substrate 2, in the thermal treatment equipment 40 as shown in drawing 5, for example, clean air, H_2 gas, The substrates 2 with which it introduced into the heat treatment chamber 41 via the gas inlet 43 for any they are, and the silicon oxide 1 was formed on the substrate supporting stand 42 with a built-in heater, such as Ar gas and N_2 gas, are carried, Heat treatment which only predetermined time (for example, 1 hour) heats this substrate 2 (not less than 100 **), and is cooled to a room temperature after that is performed. When many impurities about hydrogen are contained in the silicon oxide before heat treatment here, this silicon oxide for example, by heat-treating in clean air. For example, a reaction like **Si-O-Si**+2H ->**Si, +, and Si**+H_2O arises, and the dangling bond of silicon is newly formed. Also in Si-Si combination like **Si-Si**, by heat-treating, Si-Si combination goes out and the dangling bond of a silicon atom is formed like **Si-Si**->**Si, +, and

Si**. That is, in the manufacturing method of this embodiment, the number of dangling bonds is thermally stabilized by heat-treating.

[0017]The thermal treatment equipment should just be a device which does not limit to the composition of drawing 5 and can heat-treat. After a heat treatment process is completed, silicon oxide electret is formed by electrifying the silicon oxide 1 electrically. You make it charged by turning an electron beam to silicon oxide, irradiating with it from an electron gun, and introducing an electron into silicon oxide as a concrete electrifying method, as shown, for example in drawing 6. In the electrification unit which consists of the conductive wire 13 as shown, for example in drawing 7, the covering 14 of the conductive wire 13, the grid 16, and the conductive support member 15 as another electrifying method, You make it charged by adjusting charge quantity by voltage V_0 of the grid 16, and introducing into the silicon oxide 1 of the conductive support member 15 upper part the electric charge generated in corona discharge from the conductive wire 13 of the voltage V. Voltage V_0 impressed to the voltage V impressed to the conductive wire 13 and the grid 16 here is -7000 volts and about -200 volts, respectively, for example. By the way, since the charged silicon oxide 1 has a dangling bond of a silicon atom, when performing positive electrification, the trap of the positive charge is carried out to a dangling bond, for example like **Si and -> **Si^+. That is, when the dangling bond exists, the electronic state in a gap is made near Fermi energy. An electric charge is electrically fixed to the electron energy level of this electronic state, and it is got blocked, The trap of the electric charge is carried out to a dangling bond, as a result if a high temperature is not applied, it is not discharged, but heat resistance is good and the silicon oxide electret with which electric charge holding power has the long lasting large electret characteristic is obtained.

[0018]By the way, in the silicon oxide (it has life of order for several years) electret excellent in the long-term stability formed with the above-mentioned manufacturing method, The number of oxygen atoms was the abbreviated 1.7 time of the number of silicon atoms, and the dangling bond density of the silicon atom which combines with three oxygen and has a dangling bond was for example, abbreviated $1.4x10^{18}cm^{-3}$. As for dangling bond density, it is desirable that they are abbreviated $10^{13}cm^{-3}$ thru/or abbreviated $10^{19}cm^{-3}$. The number of oxygen atoms and the number of silicon atoms use here the value calculated by the SIMS (Secondary Ion Mass Spectroscopy) method. Dangling bond density uses the value calculated by the ESR (Electron SpinResonanse) method. It is checking by the SIMS method that this silicon oxide electret is carrying out the abbreviated 1 atomic-ratio owner of the impurity of abbreviated 10 atomic ratios and nitrogen for the impurity of hydrogen. In order to enter in the form which carried out electrification and to fulfill neutrality condition, the dangling bond of silicon carries out electrification of a part of H or N, and it is considered that an electric charge is fixed to a dangling bond.

[0019]The sectional side elevation of sound devices, such as a microphone or an earphone constituted using the silicon oxide electret of the above-mentioned composition, is shown in drawing 8. The member 18 which the sectional shape by which, as for this sound device, sectional shape is stored in the abbreviated C character-like metal casing 17 and the metal casing 17 becomes from an insulating material by the shape of an abbreviated U character, The diaphragm electrode 5 which consists of the fixed electrode 19 which consists of a metal plate fixed to the both ends of the member 18, and a metallic

foil which counters with the fixed electrode 19 on both sides of the washer ring 20 which consists of insulating materials, and is arranged in parallel, and vibrates with sound pressure, It has the fixed electrode 19 of the diaphragm electrode 5, and silicon oxide electret 1' currently formed in the surface of the side which counters, and the diaphragm electrode 5 is electrically connected to the case 17 via the ring 23 which consists of electrical conducting materials. It is electrically connected to the pins 21 and 22, respectively, and the metal casing 17 and the fixed electrode 19 can be connected to an external electric circuit via the pins 21 and 22. Here, an air layer is made between silicon oxide electret 1' and the fixed electrode 19. This sound device For this reason, when [for example,] it uses as a microphone and power supply voltage is supplied via the pins 21 and 22, While the diaphragm electrode 5 vibrates and an electrode spacing (distance of the diaphragm electrode 5 and the fixed electrode 19) changes with sound pressure, electric capacity changes, and the voltage produced at this time is taken out as an audio signal via the pins 21 and 22. Since Coulomb force inter-electrode [each] is strengthened by providing silicon oxide electret 1', sensitivity can be raised when using as a microphone.

[0020]By the way, since the thickness of silicon oxide electret 1' is formed in the thin film (0.5 micrometer - about 3 micrometers), the above-mentioned sound device can make an electrode spacing small, and can enlarge change of the electric capacity by vibration of the diaphragm electrode 5. Silicon oxide electret 1' may not limit forming in the diaphragm electrode 5, and may form it in the diaphragm electrode 5 of the fixed electrode 19, and the surface of the side which counters, and the silicon substrate by which the high-concentration impurity was added may be used for it as the stationary-plate electrode 19 in this case.

[0021]

[Effect of the Invention]Since the silicon atom which combines with three oxygen atoms and has a dangling bond in silicon oxide to achieve the above objects exists, the invention of claim 1, When the dangling bond exists, the electronic state in a gap is made near the Fermi energy of the approximately center of a band gap, Since an electric charge is electrically fixed to the dangling bond which is making the electron energy level of this electronic state as a result, it is effective in the ability to provide silicon oxide electret good [heat resistance] and long lasting.

[0022]Since the dangling bond densities are abbreviated $10^{15}cm^{-3}$ thru/or abbreviated $10^{19}cm^{-3}$, the invention of claim 2, The electron energy level of this electronic state is made near the Fermi energy, An electric charge is electrically fixed to the dangling bond which is making the electron energy level of this electronic state, and, as a result, it is effective in the ability to provide silicon oxide electret good [heat resistance] and long lasting.

[0023]Since the invention of claim 3 is twice [less than] the number of silicon atoms, the number of oxygen atoms, By forming the dangling bond of silicon, the electronic state in a gap is made near the Fermi energy of the approximately center of a band gap, An electric charge is electrically fixed to the dangling bond which is making the electron energy level of this electronic state, and, as a result, it is effective in the ability to provide silicon oxide electret good [heat resistance] and long lasting.

[0024]Since the invention of claim 4 is the abbreviated 1.7 time of the number of silicon atoms, the number of oxygen atoms, An electric charge is electrically fixed to the dangling bond which the number of silicon atoms becomes superfluous to an oxygen

atom, a dangling bond is formed, and the electronic state in a gap is made near the Fermi energy of the approximately center of a band gap, and is making the electron energy level of this electronic state. As a result, it is effective in the ability to provide silicon oxide electret good [heat resistance] and long lasting.

[0025]In the invention of claim 1, since the invention of claim 5 contains hydrogen or nitrogen, it can increase a dyeing ring bond by heat-treating. In the invention of claim 3, since the invention of claim 6 is carrying out the abbreviated 1 atomic-ratio owner of the impurity of abbreviated 10 atomic ratios and nitrogen, the impurity of hydrogen. In order a part of H and N are contained in the form which carried out electrification and to fulfill neutrality condition, the dangling bond of silicon carries out electrification and an electric charge is fixed to a dangling bond. As a result, it is effective in the ability to provide silicon oxide electret good [heat resistance] and long lasting.